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ROYAL AIRCRAFT ESTABLISHMENT

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TECHNICAL NOTE No: MET.227

IMPURITIES IN TITANIUM:

PHOSPHORUS

by

D.A.SUTCLIFFE

SEPTEMBER, 1955

MINISTRY OF SUPPLY, LONDON, W.C.2

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September, 1955

ROYAL AIRCRAFT ESTABLISHMENT, FARNBOROUGH

Impurities in Titanium : Phosphorus

by

D. A. Sutcliffe

RAE Ref: Met M3/M10652/DAS

SUMMARY

Binary titanium phosphorus alloys containing up to 3.8% phosphorus have been prepared by arc melting. All the alloys have been hardness tested; tensile and impact tests have been made at room temperature on the alloys containing up to 1.13% phosphorus. The results show that the addition of 0.25% phosphorus causes a marked rise in hardness and tensile strength with a corresponding loss in percentage elongation and impact strength. Further additions of phosphorus up to 1.13% caused a continuation of these trends though not so rapidly as at first. Titanium phosphorus alloys in the "as cast" condition exhibited a eutectic structure.

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1 Introduction

In a previous note[1] the possible sources of contamination of titanium during its preparation have been discussed. The main industrial processes for the production of titanium use titanium tetrachloride and either magnesium or sodium as the reducing agent. Distilled titanium tetrachloride has been found[2] to contain less than 15 p.p.m. of phosphorus. Sulphur contents of commercial sodium have been quoted[3] as 50 p.p.m., but it was stated that the contamination by phosphorus of sodium distilled in the temperature range 573°-723°K would be negligible. Electrolytic magnesium contains approximately 0.01% P and Thermal magnesium < 0.001% P[4]; however, most of this phosphorus could be removed if necessary.

Although, at present, phosphorus is only considered to be a minor contaminant in titanium, it is of interest to those concerned with the production of the metal and the development of new methods of preparation to know what effect phosphorus has on its properties.

This note was written to bring together the results contained in published work and the results of tests at the Royal Aircraft Establishment on the effect of phosphorus on the properties of titanium. The effect on titanium alloys is not dealt with.

2 Survey of Literature

2.1 Phase Diagram

No complete or partial phase diagram of the titanium phosphorus system has yet been published. However, the existence of the following phosphides has been claimed; Ti_2P[5]; TiP[6] and TiP_2[7].

In a series of alloys prepared[8] by melting magnesium reduced titanium sponge and a master alloy containing phosphorus in an argon arc furnace, it was found that intermediate phases appeared in the microstructure of specimens containing as little as 0.07% phosphorus.

2.2 Mechanical Properties

The only published results on the effect of phosphorus on the mechanical properties of titanium are those of Goldhoff and Others[8]. They prepared a series of alloys as described in paragraph 2.1; these were forged at 955°C to $1\frac{1}{8}$" square bar and then hot rolled at 790°C to $\frac{7}{8}$" diameter round bar. They were annealed at 790°C for $\frac{1}{2}$ hour before testing. The results of the tests are given graphically in Fig.1. From these results it may be seen that phosphorus additions up to 0.4% brought about a small increase in the tensile strength of titanium but had little effect on the percentage elongation.

The titanium used in these experiments was not of very high purity, the results quoted did not include impact and hardness tests, and the range of alloys studied was limited to a maximum phosphorus content of 0.4%. In view of these factors it was considered desirable to repeat the experiments and to extend the scope of the work. Accordingly, a series of alloys was prepared and tested.

3 Preparation of Specimens

The alloys were prepared by arc melting using a technique described[9] previously.

The starting materials were:

Titanium: DuPont sponge, which when melted had a hardness of 133 D.P.N. Its chemical analysis and mechanical properties have been reported[9] already.

Phosphorus: red phosphorus of German origin supplied by H. Schering & Co. was used.

The phosphorus was added to the melt in the form of a master alloy, which was prepared by heating a mixture of phosphorus and titanium sponge < ⅛" in a sealed evacuated silica tube at 750°C for 48 hours. The reaction products were then mixed with more titanium and melted in the arc furnace to give a master alloy containing 2 to 3% phosphorus; this was added to titanium to give alloys of the required phosphorus content. (0 to 1.13%). The actual compositions obtained were close to the intended values indicating that the phosphorus loss on melting was slight.

The arc melted ingots weighed approximately 60 gms and were hot worked by forging and rolling down to 0.3" square bars. All the ingots could be worked satisfactorily although there was a marked increase in resistance to deformation as the phosphorus content increased. From these bars, tensile and sub-standard Izod test pieces could be machined. After machining, all test pieces were annealed for 1 hour in air at 650°C.

The homogeneity of the bars was tested by making chemical analyses at points along their lengths, hardness tests and microscopical examination; the results showed the homogeneity to be good in general, but in the case of the 1.13% P alloy a certain amount of segregation was detected.

4 Results

4.1 Hardness Tests

The results are given in Table I; in the case of the high phosphorus (> 1.13%) alloys each value is the average of three impressions; all the other results are the average of at least five impressions; the scatter in the values was low and even the alloy containing 1.13% P which showed segregation in the microstructure had a scatter of less than plus or minus 5%.

TABLE I

Hardness Test Results

% P	<0.01	0.09	0.14	0.18	0.37	0.66	0.85	1.13	1.91	2.31	2.75	2.96	3.8
"As Cast"	133					194	214	242	283	277.5	325	328	398.5
Worked and Annealed	133	153	167	167	192	209.7	215	242					

The addition of phosphorus up to 0.66% to titanium brings about a rapid increase in hardness, further additions up to the limit tested (3.8% P) cause a steady but not so rapid increase.

4.2 Tensile Tests

The tensile tests were made on ¼" B.S.F. test pieces in a 5½ ton Denison testing machine using the load range 0 to 2400 lb.

The results are given in Table II and are presented graphically in Fig.2. All values are the average of three tests. The amount of scatter was small and in the worst case (1.13% P) the results were within ±2 tons/sq in. of the average.

TABLE II

Tensile Test Results

% P	<0.01	0.09	0.14	0.18	0.37	0.66	0.85	1.13
P.L. Tons/sq in.	9.3	8.6	11.8	9.5	15.6	12.6	15.3	11.7
0.1% P.S. " "	18.5	16.6	21.4	20.2	24.8	24.1	26.6	28.0
0.2% " " "	19.5	18.2	22.8	21.4	25.6	25.4	28.1	30.3
0.5% " " "	20.4	20.1	24.3	22.9	26.4	27.8	30.5	33.1
T.S. " "	25.5	27.4	31.0	30.5	34.4	36.7	39.1	41.2
$E \times 10^{-6}$ lb/sq in.	15.6	16.0	16.2	16.0	16.1	16.6	16.5	16.7
Elongation on $4\sqrt{A}$ %	50	44	34	35	29	26.7	22.5	16.7

The tensile strength developed increases rapidly with the addition of up to 0.37% phosphorus and then less rapidly up to 1.13% phosphorus. The percentage elongation drops rapidly at first, and then less rapidly, corresponding to the increase in tensile strength. There is an initial drop in proof stress values, then these nearly follow the trend in the tensile strength.

Phosphorus increases the Young's Modulus of titanium continuously but slightly over the range of phosphorus contents studied.

4.3 Izod Tests

The effect of additions of phosphorus on the impact strength of titanium was determined on subsidiary standard Izod test pieces (5 mm × 5mm × 67 mm) using a striking energy of 10 ft lb.

The results of the tests are given in Table III and graphically in Fig.3.

TABLE III

Izod Test Results

% P	0.01	0.09	0.14	0.18	0.37	0.66	0.85	1.13
Sub Standard Izod		2.5	2.0	2.9	2.3	0.9	1.0	0.5
	8.0	2.3	1.9	2.9	2.2	1.1	1.0	0.5
(10 ft lb) ft lb		2.4	2.0	2.7	2.4	1.0	1.0	0.5

Phosphorus caused an initial sharp drop in impact strength, the value of which dropped from 8 to 2.4 ft lb on the addition of 0.09% phosphorus. The impact strength then decreased steadily but less sharply with further additions of phosphorus.

4.4 Metallographic Examination

Specimens of each composition were prepared for microscopic examination and a representative selection of photomicrographs are given in Figs.4 to 8. Fig.4 gives some idea of the amount of second phase present in alloys containing as little as 0.09% phosphorus and it also shows the tendency for the second phase to form along grain boundaries. In the alloy containing 0.37% P (Fig.5) can be seen the well established rivers of second phase along the grain boundaries. In the as cast master alloy (Fig.6) a marked eutectic structure was observed; a photograph X750 (Fig.7) of another master alloy shows in more detail the duplex structure of the eutectic. The network of second phase could be broken down quite readily by working and annealing; this is shown in Fig.8.

The formation of a complete network of second phase along the grain boundaries on solidification would detract from the weldability of alloys containing more than 0.15% phosphorus.

5 Conclusions

From the results obtained in the present investigation and the literature, certain conclusions regarding the effect of phosphorus on titanium may be made.

(1) An alloy of titanium and phosphorus may be melted in an arc furnace without appreciable loss of phosphorus, so phosphorus contamination of titanium sponge may pass into the melted product.

(2) Arc melted titanium alloys containing up to 1.13% phosphorus may be successfully hot worked.

(3) Titanium phosphorus alloys up to at least 1.13% P can be satisfactorily machined, milled, threaded and sawn.

(4) At room temperature the addition of 0.25% phosphorus to titanium causes a sharp increase in the tensile strength and hardness. Further additions of phosphorus up to 1.13% cause a less rapid increase in these properties.

(5) There is a rapid drop in percentage elongation on the addition of phosphorus, but alloys containing less than 0.95% P have an elongation greater than 20%.

(6) The addition of phosphorus (up to 1.13%) brings about a 7% increase in the Young's Modulus of titanium.

(7) After a large drop in impact strength on the addition 0.15% P, further additions of phosphorus (up to 1.13%) cause a less rapid though steady fall in the impact strength of titanium.

(8) Intermediate phases have been noted in the microstructure of titanium containing as little as 0.07% phosphorus.

(9) As a single impurity phosphorus could be tolerated up to 0.95% from a consideration of tensile results, with a 20% elongation as the minimum requirement. However, alloys containing this quantity of phosphorus would have low impact strengths, and possibly poor weldability and cold formability as well.

(10) Titanium phosphorus alloys solidify with a eutectic reaction.

Acknowledgments

The author thanks his colleagues for their help at all stages of the work.

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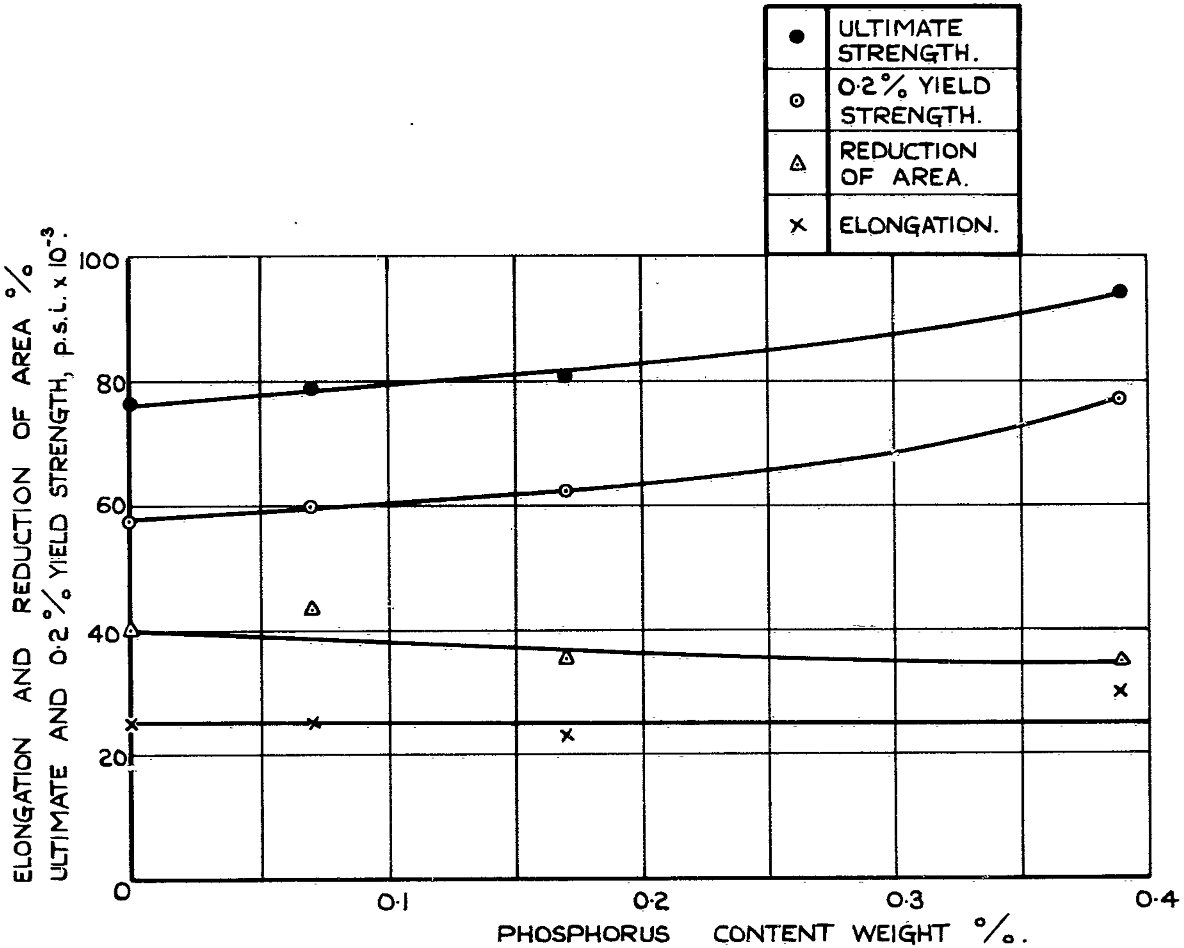

FIG.1. EFFECT OF PHOSPHORUS ON PROPERTIES OF TITANIUM. (GOLDHOFF)

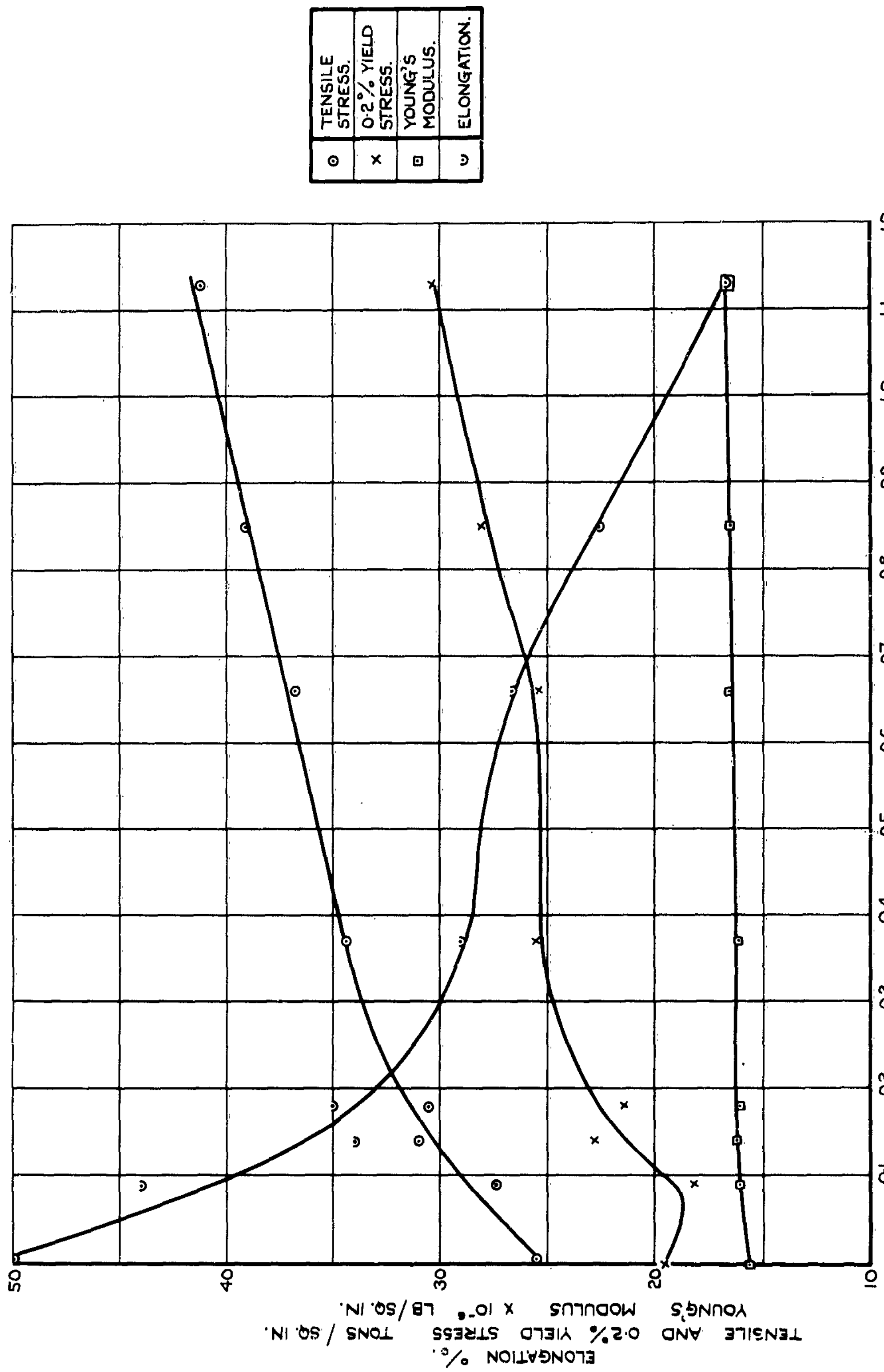

FIG. 2. TENSILE TEST RESULTS.

MAT. 15038.

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FIG. 3

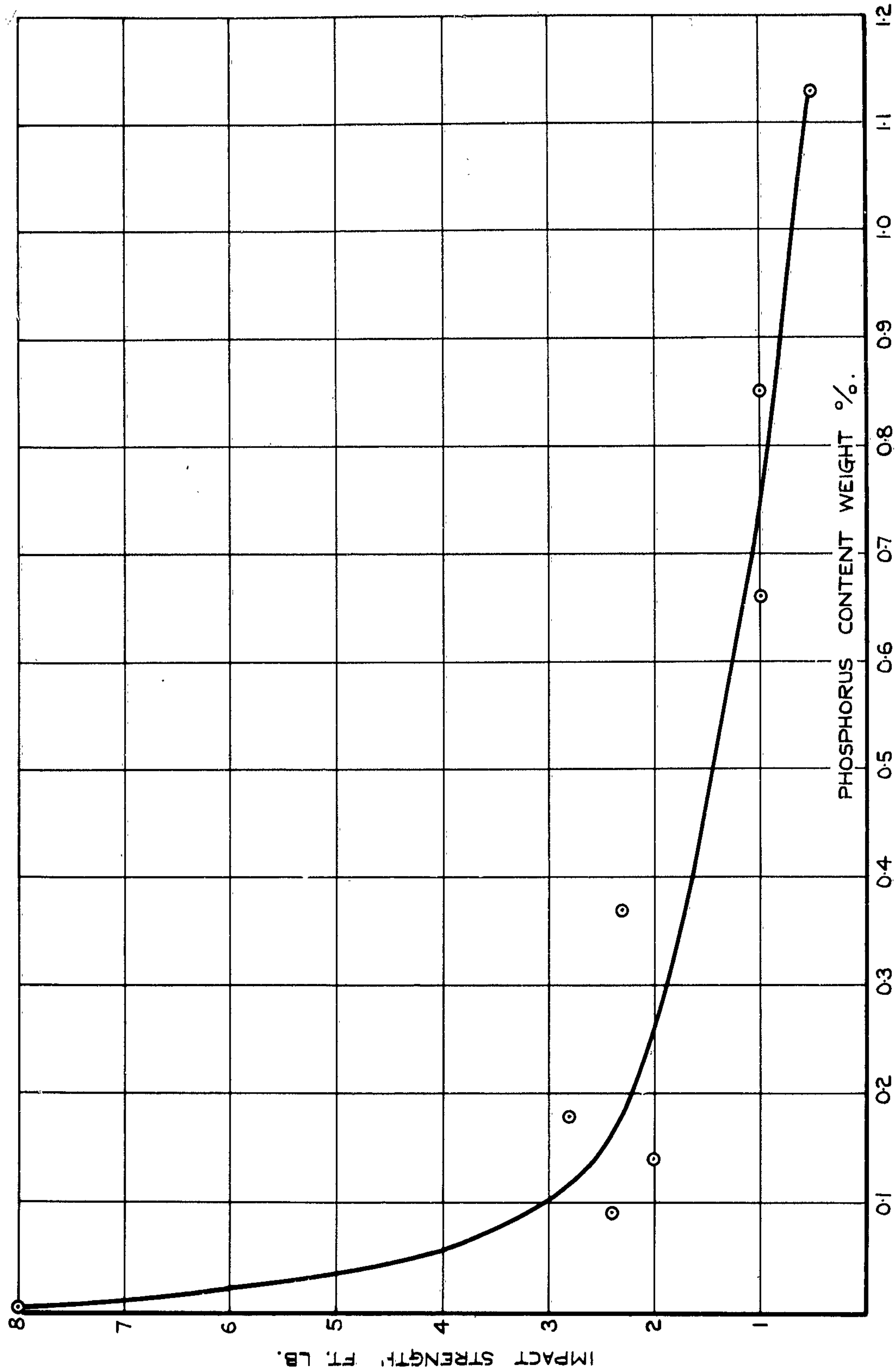
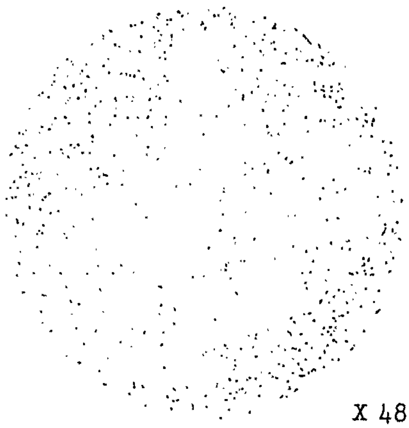


FIG 3 IMPACT TEST RESULTS (SUB STANDARD SPECIMENS)

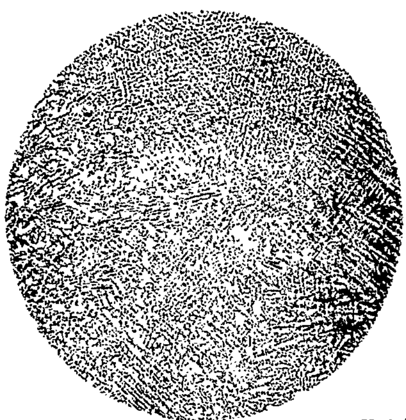


X 48

Fig.4 0.09% P. Alloy
"As Cast"

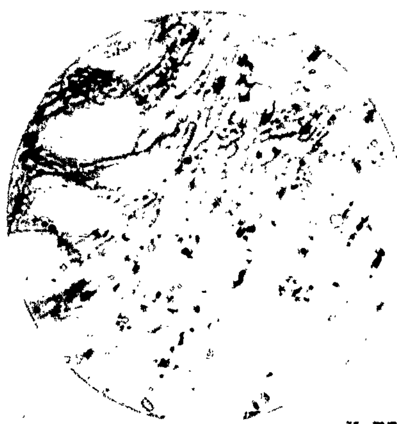
X 48

Fig.5 0.37% P. Alloy
"As Cast"



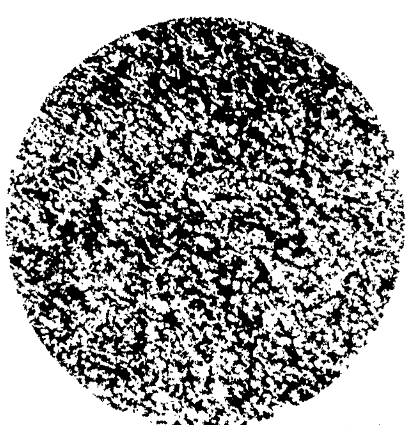
X 48

Fig.6 3.8% P. Alloy
"As Cast"



X 750

Fig.7 2.31% P. Alloy
"As Cast"



X 100

Fig.8 0.66% P. Alloy
Worked & Annealed.

FIG.4 - 8 TITANIUM-PHOSPHORUS SERIES

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